Analytical Methods for Detection and Quantitation of Explosives Residues

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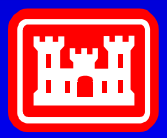

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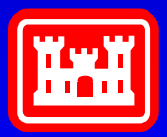
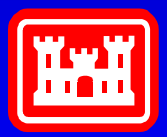
Analytical Techniques

- High Performance Liquid Chromatography with UV detection (HPLC-UVD)
- Gas Chromatography with Electron Capture Detection (GC-ECD)
- Liquid Chromatography coupled with Mass Spectrometry (LC/MS)
- Gas Chromatography with Mass Selective Detection (GC/MSD)



Extraction Techniques

- Sonication - soils and sediments
- Direct injection - aqueous samples
- Salt-out extraction - aqueous samples
- Solid Phase Extraction - aqueous samples
- Solid Phase Microextraction (SPME) – aqueous samples

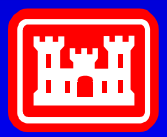


Analytical Methods

- SW-846 Method 8330 (current “gold standard”) uses dual column reverse phase HPLC with UV detection.
- SW-846 Method 8095 (Update IV) uses dual column high resolution GC with electron capture detection.
- Development work underway with LC/MS using Method 8321
- Possible role for GC/MS using modified Method 8270

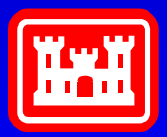
SW-846 Methods

- Method 8330 - Nitroaromatics & nitramines by HPLC
- Method 8331 – Tetrazene by HPLC
- Method 8332 – Nitroglycerine by HPLC
- Method 8095 – Explosives by GC
- Method 8091 – Nitroaromatic & cyclic ketones by GC
- Method 8321 – Solvent extractable nonvolatile compounds by HPLC/TS/MS or HPLC/UVD
- Method 3535 – Solid Phase Extraction



Method 8330

- Current “gold standard” developed by Tom Jenkins *et al.* at CRREL in late 1980’s
- Dual column reverse phase (C-18 & CN) HPLC with UV detection
- Broad range of nitroaromatics and nitramines
- Direct injection of aqueous samples
- HPLC accurately quantitates extract concentrations as low as 20 ppb
- Aqueous DLs ~20 ppt when coupled with SPE (Method 3535)



Explosives Currently Analyzed by HPLC at ECB

- Method 8330 targets: HMX; RDX; 1,3,5-TNB; 1,3-DNB; Tetryl; NB; TNT; 4ADNT; 2ADNT; 2,4-DNT; 2,6-DNT; 2-NT; 3-NT; 4-NT
- PETN; Picric Acid; Nitroglycerine; CL-20
- TNT metabolites Azoxytoluenes, Diaminonitrotoluenes & Triaminotoluenes
- Nitroso metabolites of RDX (MNX,DNX,TNX) & HMX (MN-HMX)

Method 8095

- Relatively new developmental standard method appears in Update IV of SW-846
- Dual capillary column GC with electron capture detection
- Instrument accurately quantitates extract concentrations as low 1 ppb for some targets
- Aqueous DLs ~1 ppt when coupled with SPE (Method 3535)
- Incorporates a surrogate; ECB uses 3,4 DNT
- Targets: HMX; RDX; 1,3,5-TNB; 1,3-DNB; Tetryl; NB; TNT; 4ADNT; 2ADNT; 2,4-DNT; 2,6-DNT; 2-NT; 3-NT; 4-NT; 3,5-DNA; PETN; NG

Method 8095 Technical Issues

- Thermally labile explosives don't like hot GC injection ports and ovens
- HMX is very unstable; currently only one analytical column gives reproducible chromatography
- PETN also problematic giving poor chromatography with possible thermal degradation
- Cleanup techniques for extracts need to be developed
- Need frequent cleaning of GC injection port to minimize degradation
- Stability of low-level explosives concentrations in sample extracts

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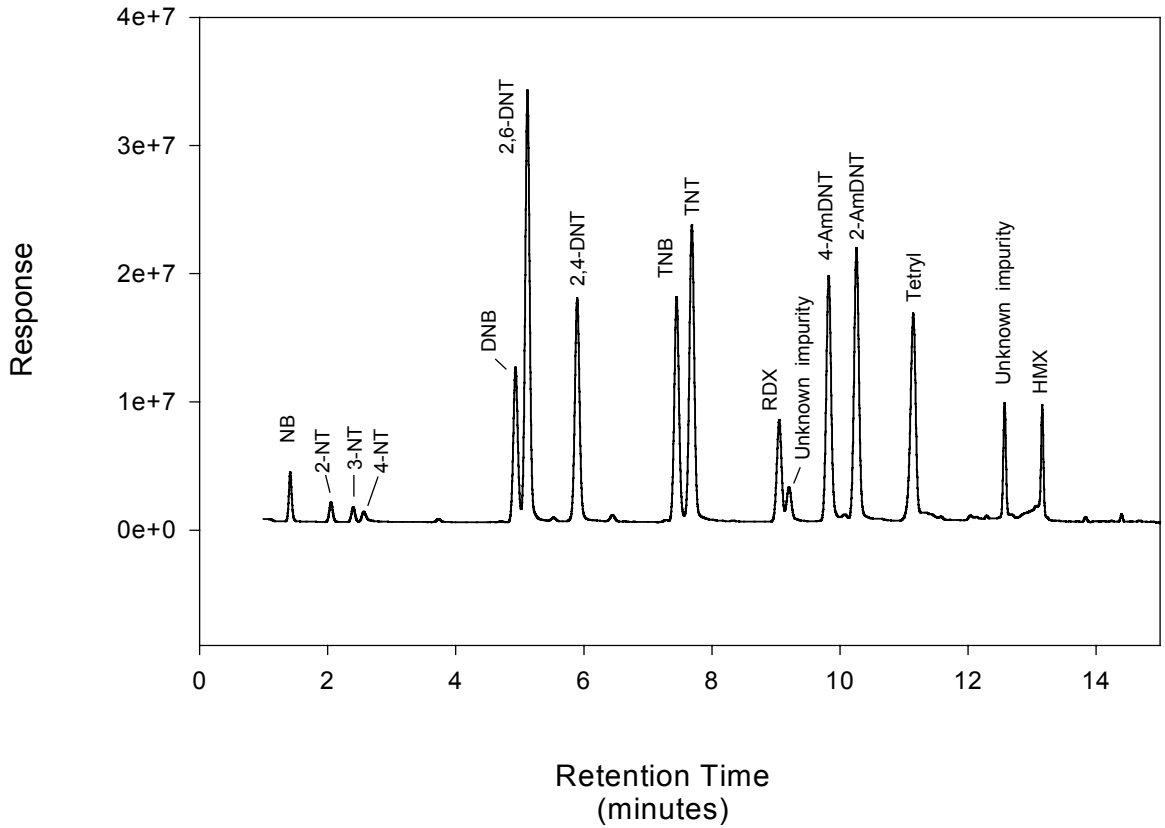
Explosives by GC/ECD
(Restek Rtx-TNT Capillary Column)



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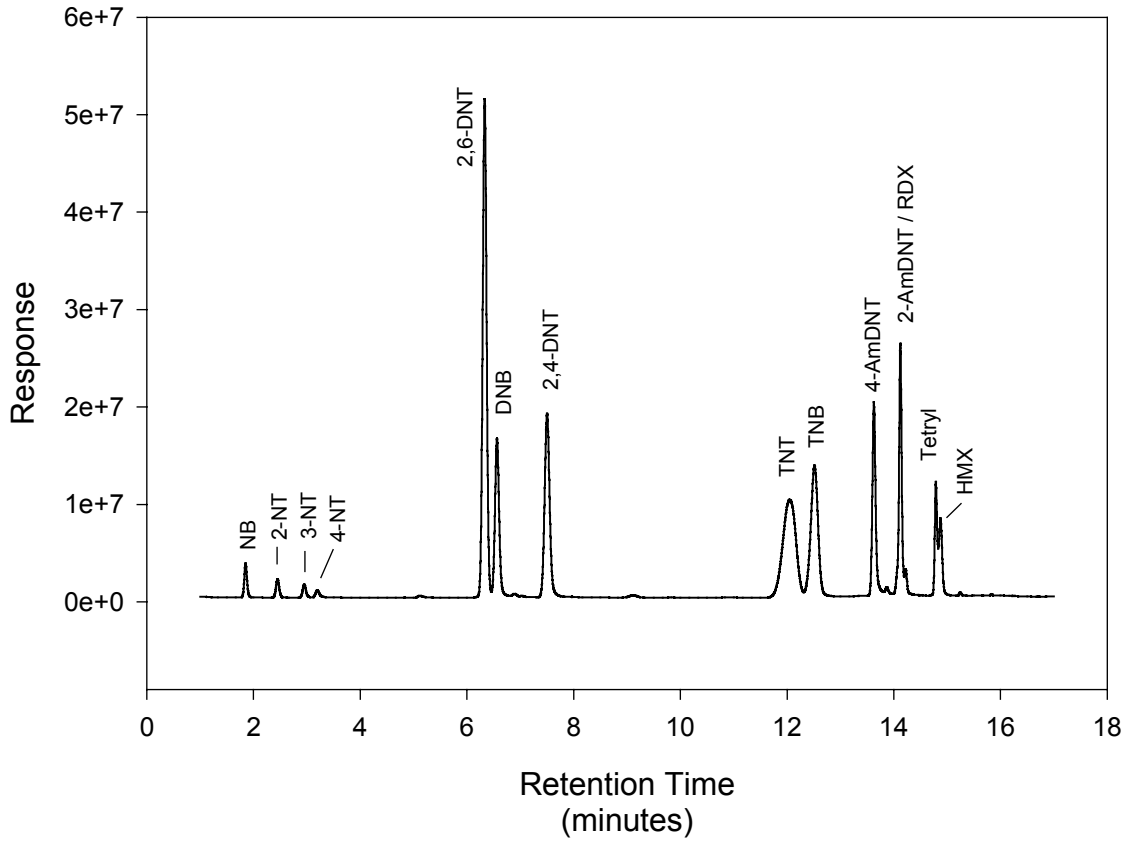
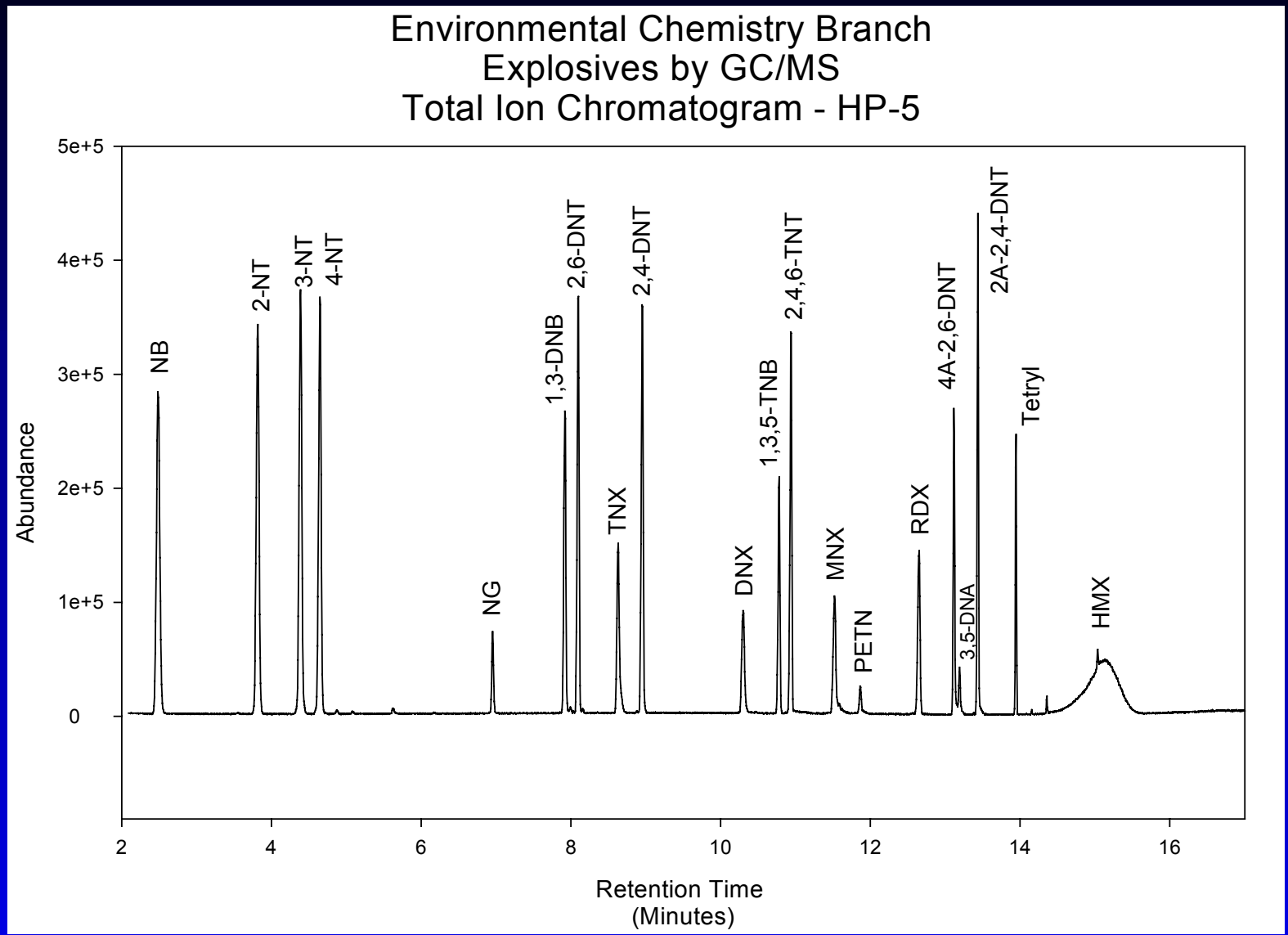
Explosives by GC/ECD
(Restek Rtx-TNT2 Capillary Column)



Explosives Analysis By GC/MSD

- Potential advantages
  - → identification of unknowns when in SCAN mode
  - → single analytical column
  - → low detection limits (~ 100 ppb) in SIM mode
- Disadvantages
  - → degradation of thermally labile compounds (HMX)
  - → high flow rates present problems with MS vacuum
  - → relatively high detection limits in SCAN mode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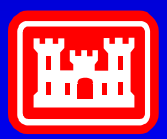
Explosives by GC/MS
Total Ion Chromatogram - HP-5
Abundance
5e+5
4e+5
3e+5
2e+5
1e+5
0
NB
2-NT
3-NT
4-NT
NG
1,3-DNB
2,6-DNT
TNX
2,4-DNT
DNX
1,3,5-TNB
2,4,6-TNT
MNX
PETN
RDX
4A-2,6-DNT
3,5-DNA
2A-2,4-DNT
Tetryl
HMX
2
4
6
8
10
12
14
16
Retention Time
(Minutes)

Explosives by LC/MS

- For routine analytical work Method 8321 can be used for method development
- Mixtures separated into components by LC providing retention time data prior to introduction into MS
- Both SCAN and SIM modes can be used
- Can be coupled with UV detection
- Low detection limits
- Identification of unknowns compounds for which analytical standards are not commercially available

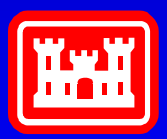


Explosives by LC/MS

- ECB's ThermoFinnigan system includes
  → LC/MS - LCQ Deca
  → Autosampler - Spectrasystem AS3000
  → LC Detector – Spectrasystem UV6000
  → Software – Xcalibur data system
- MS detector can operate in ESI (Method 8321) or APCI mode
- MS/MS analysis is two-stage process identifying characteristic fragment ion upon activation of isolated precursor ion
  → allows identification of targets in complex matrices
- Sample can be introduced by direct infusion without using LC for separation; mainly for research applications

Explosives by LC/MS

- Probably not a viable solution for routine analytical
- Relatively expensive
- Can be useful with problem samples
- Good tool for research
- Valuable for qualitative analysis of unknowns
- Can be used for confirmation when not possible by HPLC alone



Detection Limits

- Regulatory limits or project specific requirements dictate detection limits needed
- Influenced by sample matrix, nature of target compound, sample prep & analytical techniques
- Sample prep: Concentration techniques

  → 1L water sample → 10 mL SPE extract → 20 uL microconcentrate = 50,000:1
- Analytical technique sensitivity:

  GC/ECD > HPLC/UVD > GC/MS or LC/MS (SIM) > GC/MS or LC/MS (SCAN)

Summary

- HPLC → mature methodology; good sensitivity; ECB's broadest range of targets
- GC → developing technology; currently offers highest sensitivity; techniques need to be honed
- GC/MSD → offers some advantages to GC & HPLC; probably not viable for routine analysis of explosives
- LC/MS → useful for problem samples & research applications; sensitive & selective; probably not viable for routine analysis of explosives

Environmental Chemistry Branch Mission

- Quality assurance: split sample quality assurance analysis, technical assistance, and problem solving to support USACE environmental HTRW programs
- Analytical chemistry support: water quality analysis and in-house HTRW project analysis
- Research: DOD relevant topics
- Research support: chemical analysis and chemistry technical support for ERDC research

Environmental Chemistry Branch Resources

- Personnel: 31 Federal Government employees, 4 contract employees, 14 contract students
- Branch Chief: Doug Taggart
- Four team leaders: Dave Splichal, Prem Arora, Laura Percifield, and Bobby Jones
- Equipment: all major routine analytical equipment plus specialized equipment such as ICP/MS, LC/MS
- Excellent analytical chemistry facilities in two locations

Standard Analytical Chemistry Capabilities

- Volatile and semivolatile organics by GC/MS
- Pesticides and herbicides by GC
- Metals by ICP, ICP/MS, and GFAA
- Nutrients and anions by ion chromatography and autoanalyzers
- Explosives by HPLC
- Petroleum hydrocarbons by GC
- Polychlorinated biphenyls (PCBs) by GC

Specialized Analytical Capabilities

- Metals by ICP/MS
- PCB congeners
- Low-level PAHs by GC/MS (SIM)
- Explosives (TNT and RDX) breakdown products analysis by HPLC
- White phosphorus
- Metals speciation (As, Fe, Cr, Hg)
- Other methods under development: LC/MS of explosives, perchlorate by IC, methyl mercury, explosives by GC/ECD, tributyl tin by GC

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